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# High pressure structure of half-metallic CrO<sub>2</sub>

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Evidence for a structural phase transition from rutile  $\alpha$ -CrO<sub>2</sub> phase I ( $P4_2/mnm$ ) to orthorhombic  $\beta$ -CrO<sub>2</sub> phase II (CaCl<sub>2</sub>-like,  $Pnmm$ ) is presented using angle-resolved synchrotron x-ray diffraction and high sensitivity confocal Raman spectroscopy. The transition to the CaCl<sub>2</sub> structure, which appears to be second-order, occurs at  $12 \pm 3$  GPa without any measurable discontinuity in volume, but is accompanied by an apparent *increase* in compressibility. Raman data are also presented to show further evidence for a second-order structural phase transition as well to demonstrate soft-mode behavior of the B<sub>1g</sub> phonon mode.

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## 1. Introduction

Chromium dioxide ( $\text{CrO}_2$ ) has many properties of interest to both the scientific community and industry. It was first introduced as a magnetic recording media in 1974 mainly due to its relatively high coercivity but has received much more recent attention for its unique electronic properties. First suggested to be half-metallic by Schwarz<sup>1</sup>,  $\text{CrO}_2$  has been studied extensively both theoretically and experimentally and has been shown to possess near 100% spin polarization at the Fermi level using superconducting point-contact tunneling experiments.<sup>2</sup> Its half-metallic behavior gives rise to relatively low electrical resistivity for an oxide,  $\sim 300 \mu\Omega\text{-cm}$  (Ref. 3), and is commonly referred to as a “bad metal”.  $\text{CrO}_2$  is also ferromagnetic at room temperature with a high Curie temperature of  $T_c = 390 \text{ K}$  relative to other candidate half-metals. These two properties, along with its already wide availability, make  $\text{CrO}_2$  scientifically and technologically important and an ideal material for developing spintronic devices.

$\text{CrO}_2$  is also one of the simplest known half-metals and crystallizes into the rutile structure at ambient conditions, a structure commonly found in many metal dioxides ( $\text{MO}_2$ ;  $M = \text{Ti, Cr, Mn, Sn, Ge, Pb, etc.}$ ). The rutile structure consists of tetragonally distorted edge-sharing  $\text{MO}_6$  octahedra (see Fig. 1), one of the most fundamental building blocks of covalently bonded network structures found in hard materials and earth minerals like stishovite. Larger metal ions (ie,  $M = \text{W, Re, Mo, etc.}$ ), however, tend to form an eight-fold coordinated calcite ( $\text{CaF}_2$ ) structure while smaller ions ( $M = \text{C, Si, etc.}$ ) crystallize into a four-fold coordinated tetrahedral structure. At high pressures, the rutile structure typically transforms to another six-fold coordinated structure,  $\text{CaCl}_2$ , or the  $\alpha\text{-PbO}_2$  structure found in shock compressed  $\text{SiO}_2$  and known as a post-stishovite structure.<sup>4</sup> The smaller four-fold coordinated  $\text{SiO}_2$  transforms into the six-fold rutile structure, stishovite. Therefore, to the first approximation these pressure-induced structural transitions may be understood in the simple view of topological packing of hard spheres, i.e. an increase in the coordination number and the associated electrostatic

interaction at high densities. At high pressures, however, the electronic structure also changes in a significant way and so does the nature of electron interaction, becoming more repulsive and dominated by electron kinetic energy. As a result, the characteristics of these MO<sub>2</sub> transitions could be more complex than is evident from their rather continuous manner, occurring without any structural or volume discontinuity. The rutile structure has even been found in the molecular solid CO<sub>2</sub>-II at high pressures and temperatures.<sup>5</sup> Furthermore, the electronic contribution to structural stability is significant in transition metal oxides at high pressures, as is evident from the Mott insulator-metal transitions<sup>6,7</sup>, charge transfer transitions<sup>8</sup>, valence transitions, etc.

In the present work, we present a high-pressure structural study of CrO<sub>2</sub> using synchrotron x-ray diffraction and Raman spectroscopy. Evidence for a second-order structural transition at  $12 \pm 3$  GPa from rutile  $\alpha$ -CrO<sub>2</sub> phase I to orthorhombic  $\beta$ -CrO<sub>2</sub> phase II, accompanied by an *increase* in compressibility, is presented as well as evidence for soft-mode behavior in the Raman spectrum. A second phase transition is also suggested from anomalies in the x-ray and Raman data around 30 GPa. Finally the transition pressure for CrO<sub>2</sub> is investigated in the context of other known rutile-CaCl<sub>2</sub> transitions at high pressure.

## 2. Experimental Procedures

Powdered  $\alpha$ -CrO<sub>2</sub> was obtained commercially under the name Magtrieve from DuPONT and loaded into Livermore-designed diamond-anvil cells(DACs) in order to achieve pressures up to 50 GPa. Two samples were prepared for x-ray diffraction experiments. One sample was loaded into a 130 micron hole in a Re gasket attached to the piston anvil of a membrane-type cell. Mineral oil was used as a pressure transmitting medium and Au powder was added for pressure determination. The other sample was loaded into the 160 micron hole of a Re gasket attached to the piston anvil of a LLL cell along with several small Ruby chips for pressure determination using the Ruby fluorescence method.<sup>35</sup> The cell was then placed into a Janis Research continuous-flow He cryostat modified for He loading into the LLL cell. Liquid He was allowed to accumulate well above the top of the cell and then the pressure was reduced in the cryostat until superfluid He was

obtained. The cell was then opened briefly to allow a small amount of liquid He to leak in and then sealed. A larger sample hole was used, as well as a thicker indentation, to allow for a ~30% volume compression of the liquid He upon loading.

Angle-dispersive x-ray diffraction (ADXRD) data was performed at beamline 16ID-B, HP-CAT at the APS at Argonne National Laboratory using  $\lambda = .3680 \text{ \AA}$  x-rays. The synchrotron x-ray beam was focused down to 12x12 microns using a pair of long (0.5 m) Kirkpatrick-Baez bimorph x-ray mirrors and the partial Debye-Scherrer rings were collected on a Mar345 image plate. Raw x-ray diffraction data was integrated with fit2D<sup>9</sup> and analyzed using XRDA and GSAS. Le Bail whole-profile fitting was used to obtain lattice parameters and profile coefficients and then a Rietveld refinement was performed to obtain internal oxygen coordinates. Background removal was done manually due to a very irregular amorphous background that was difficult to fit.

For Raman measurements, powdered CrO<sub>2</sub> along with several small Ruby chips for pressure determination was loaded into the 140 micron hole drilled in a Re gasket attached to the piston anvil of a LLL-type cell. The cell was then lightly closed and immersed in liquid argon. After the cell came into thermal equilibrium with the surrounding Ar liquid it was then opened briefly to capture a small quantity of Argon for use as the pressure transmitting medium. Mineral oil was not used due to the broad, amorphous background generated during previous Raman attempts. Helium was also not used due to the high initial loading pressures required to ensure liquid He capture.

Raman spectra were obtained using a confocal micro-Raman system designed for maximum light collection. A single stage spectrometer was used for spectra collection along with a pair of Kaiser Supernotch holographic filters for rejection of the Rayleigh scattered light. The 532 nm second harmonic of a diode pumped Nd:VO<sub>4</sub> laser was used for Raman excitation. The spot size at the sample was <10  $\mu\text{m}$ . During previous Raman attempts with a conventional Raman setup, sample heating due to the high (100-200 mW) laser powers required would cause a change in oxidation from CrO<sub>2</sub> to Cr<sub>2</sub>O<sub>3</sub>.<sup>10</sup> These high laser powers were required because the black color and half-metallic nature of the

material made the Raman scattered signal very weak. A lower laser power can be used in such a system, however the long collection times would reduce the density of data points and increase the error in pressure measurement as some cell relaxation occurs during the course of a measurement. A system with high sensitivity was needed to reduce incident laser power to <30 mW while keeping the collection time down to 5 minutes.

### A. X-ray Diffraction

At ambient conditions  $\alpha$ -CrO<sub>2</sub> crystallizes into the rutile structure ( $P4_2/mnm$ ,  $Z=2$ ) with lattice parameters  $a = b = 4.421 \text{ \AA}$  and  $c = 2.916 \text{ \AA}$ , and atomic position of Cr(2a) at (0,0,0) and O(4f) at (u,u,0) with  $u = 0.301$ .<sup>11</sup> The rutile structure, shown in Fig. 1(a)(b) consists of chains of distorted edge-sharing CrO<sub>6</sub> octahedra along the  $c$ -axis with the Cr ions forming a body-centered tetragonal lattice. This distortion can work to either flatten (apical bonds are shorter than the equatorial bonds) or elongate (apical bonds are longer than the equatorial bonds) the CrO<sub>6</sub> octahedra along their axes. The positions of the oxygen atoms are determined by the fractional coordinate,  $u$ , which sets the Cr-O distances and determines the size and nature of the distortion. Figure 2(a) shows a Rietveld refinement of  $\alpha$ -CrO<sub>2</sub> performed at 7.7 GPa showing a good agreement with the rutile structure with lattice parameters  $a = b = 4.3710(1) \text{ \AA}$  and  $c = 2.8967(1) \text{ \AA}$ , and  $u = 0.294(1)$ . At this value of  $u$  the CrO<sub>6</sub> octahedra is flattened along apical direction with Cr-O distances of 1.809  $\text{\AA}$  and 1.928  $\text{\AA}$  for the apical(2) and equatorial(4) bonds, respectively.

At 12.8 GPa an orthorhombic distortion was detected by the splitting of ( $hkl$ ) diffraction lines with  $h \neq k$  as shown in Fig. 1(b) with the split ( $hkl$ )'s shown in bold. This is consistent with the structural transition from rutile to CaCl<sub>2</sub> ( $Pnmm$ ,  $Z=2$ ) crystal structures observed in other rutile-type oxides such as MnO<sub>2</sub> (Ref. 12), RuO<sub>2</sub> (Ref. 13), SiO<sub>2</sub> (Ref. 14), GeO<sub>2</sub> (Refs. 15, 16), SnO<sub>2</sub> (Refs. 17, 18) and PbO<sub>2</sub> (Ref. 19). The CaCl<sub>2</sub> crystal structure consists of chains of distorted edge-sharing CrO<sub>6</sub> octahedra along the  $c$ -axis with the Cr ions forming a body-centered orthorhombic lattice and is shown in Fig. 1(c). The position of the oxygen atom is now described by two fractional coordinates  $u_x$  and  $u_y$ . The Reitveld refinement Fig 2(b) of  $\beta$ -CrO<sub>2</sub> at 14.0 GPa shows good agreement

with the  $\text{CaCl}_2$  structure with lattice parameters  $a = 4.3874(4) \text{ \AA}$ ,  $b = 4.2818(4) \text{ \AA}$ , and  $c = 2.8779(2) \text{ \AA}$ , and  $u_x=0.299(1)$  and  $u_y=0.272(1)$ .

Figure 3 shows lattice constants obtained using a Le Bail whole-profile fit as a function of pressure with a dotted vertical line showing the transition pressure. The diffraction data from the mineral oil sample suffered from broadening of diffraction lines above 9 GPa, due to non-hydrostatic conditions inside the sample chamber<sup>20</sup>, and made refinement difficult to converge. Therefore, we only present data below 9 GPa for this sample as shown in Fig 3. On the other hand, the diffraction data obtained using He as a pressure medium stayed well resolved up to the highest pressure obtained. Below the transition pressure the compressibility of the  $a$ -axis using mineral oil and He are very close, with the He sample showing a slightly higher compressibility. The  $c$ -axis, however, shows a much lower compressibility when using He as a pressure medium, although it is clear that both curves extrapolate back to the previously reported value at  $P = 0$ . A change in compressibility at 12.8 GPa is observed for the  $c$ -axis while the area conserving quantity  $\sqrt{ab}$  follows smoothly from the  $a$ -axis across the transition. There is also a small but apparent change in compressibility of the  $c$ -axis at  $\sim 25\text{-}30$  GPa. This change may be a signature of a second phase transition. Additional evidence supporting a second phase transition was observed in our Raman data in this pressure range and is discussed below.

The pressure vs. volume data of  $\alpha$ - and  $\beta$ - $\text{CrO}_2$  phases are plotted up to 50 GPa in Fig. 4, identifying the transition pressure  $P_c = 12.8 \pm 3$ . Below  $P_c$  the mineral oil and He data agree well, resulting in a nearly identical P-V curve. Above  $P_c$  an anomalous *increase* in the compressibility occurs. This is in contrast to most materials becoming stiffer with pressure. The experimental PV curves for  $\alpha$ - $\text{CrO}_2$  was fit to the 3<sup>rd</sup>-order Birch-Murnaghan<sup>21</sup> equation of state

$$P = \frac{3}{2} B_0 \left[ \left( \frac{V}{V_0} \right)^{\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{\frac{-5}{3}} \right] \left\{ 1 + \frac{3}{4} (B_0' - 4) \left[ \left( \frac{V}{V_0} \right)^{\frac{-2}{3}} - 1 \right] \right\} \quad (1)$$

with  $B_0' = \left( \frac{dB}{dP} \right)_{T,P=0} = 4$  and  $V_0$  fixed at the previously reported value of  $56.99 \text{ \AA}^3$  (Ref. 11) which yielded a value of  $B_0 = 239 \pm 2 \text{ GPa}$  for the zero pressure bulk modulus. The high pressure  $\beta\text{-CrO}_2$  phase was also fit to Eq. (1) yielding values of  $B_0 = 162 \pm 2 \text{ GPa}$  and  $V_0 = 58.1 \pm 1.1 \text{ \AA}^3$  for the zero-pressure bulk modulus and unit cell volume respectively. In addition, we performed Birch-Murnaghan equation of state fits for both phases while letting  $B_0'$  vary, as well as fits to the Vinet equation of state. These are shown in Fig. 3 and the numerical results of the various fits are summarized in Table I. The fits to the low pressure phase all give quite similar answers, however the differences between the various equations of state are evident in the high pressure phase. This is primarily due to the lack of data to constrain  $V_0$  as  $\beta\text{-CrO}_2$  does not exist at ambient conditions. It is clear, however, that a pronounced softening is evident irrespective of the model used to fit the compression data.

## B. Raman

The Raman signal of half-metallic  $\text{CrO}_2$  is very weak due to the metallic nature of the material which, due to a short penetration depth, results in a relatively small scattering volume and low number of scattering sites.<sup>22</sup> Nevertheless, by using a fast con-focal Raman spectroscopy system we were able to obtain relatively high quality Raman spectra from powdered  $\text{CrO}_2$ , as shown in Fig. 5, using no more than 30 mW of laser power as measured at the sample. Small features in the Raman spectra below  $200 \text{ cm}^{-1}$  are, however, obscured because of the use of two holographic notch filters used to prevent Rayleigh scattered light from entering the spectrometer, the result of which was both the introduction of some small spurious peaks and much reduced transmission below  $200 \text{ cm}^{-1}$ .

A factor group analysis gives four Raman-active modes in the rutile structure,  $\Gamma_{\text{Raman}} = E_g + A_{1g} + B_{1g} + B_{2g}$ . Previous work by Iliev *et. al.*<sup>22</sup> using polarized Raman spectroscopy on single-crystal  $\text{CrO}_2$  at ambient pressure describes these modes and determined the Raman-shifts to be  $149 \text{ cm}^{-1}$ ,  $458 \text{ cm}^{-1}$ ,  $570 \text{ cm}^{-1}$ , and  $682 \text{ cm}^{-1}$  for the  $B_{1g}$ ,

$E_g$ ,  $A_{1g}$ , and  $B_{2g}$  modes. Figure 4 shows our Raman spectra of  $\text{CrO}_2$  taken at various pressures. The three peaks at  $470\text{ cm}^{-1}$ ,  $584\text{ cm}^{-1}$ , and  $700\text{ cm}^{-1}$  shown at 2.8 GPa are associated with the  $E_g$ ,  $A_{1g}$ , and  $B_{2g}$  modes of the rutile structure. Unfortunately, we were not able to observe the Raman-active  $B_{1g}$  shear mode, which has been shown to exhibit soft-mode behavior at high pressure in other rutile- $\text{CaCl}_2$  (Refs. 14, 18) transitions, due to its very weak scattering around  $150\text{ cm}^{-1}$ .<sup>13</sup>

The expected mode behavior for a phase transition from rutile to  $\text{CaCl}_2$  is a splitting of the doubly degenerate  $E_g$  mode along with the addition of a new Raman active mode of  $B_{1g}$  symmetry.<sup>13</sup> At 12.4 GPa a new peak appears at  $470\text{ cm}^{-1}$  and the  $E_g$  mode begins to broaden. By 19.5 GPa a clear splitting of the  $E_g$  mode is observed along with an additional peak emerging at  $162\text{ cm}^{-1}$ . Mode assignments for phase II are based primarily on the correlation between rutile( $D_{4h}$ ) and  $\text{CaCl}_2$ ( $D_{2h}$ ) modes except for the new Raman-active mode of  $B_{1g}$  symmetry which is tentatively assigned to the new peak at  $470\text{ cm}^{-1}$  and assumed to be accidentally degenerate. The order of the  $B_{2g}$  and  $B_{3g}$  modes shown is arbitrary as it has been argued that the sign of the spontaneous strain,  $e_{ss} = (a - b)/(a + b)$ , determines the ordering.<sup>23</sup> Because all our experiments were done on powdered samples and not single crystals, the sign of  $e_{ss}$  is unknown. It should also be noted that a seventh, unassigned peak was observed at 33 GPa, identified with an asterisk, showing a variation with pressure consistent with the other, identified peaks. The small peak around  $185\text{ cm}^{-1}$  at 41.1 GPa, marked with a cross in Fig. 4, was intermittent and did not seem to show any consistent behavior with pressure. This peak is therefore attributed to spurious noise caused by the pair of holographic notch filters coupled with the background subtraction procedure.

Figure 6 shows the pressure-induced shifts of the observed Raman modes for  $\alpha$ - and  $\beta$ - $\text{CrO}_2$ . Although we were unable to directly observe any mode-softening behavior due to the weakness of the  $B_{1g}$  shear mode in rutile  $\alpha$ - $\text{CrO}_2$ , we can speculate that in order for the  $B_{1g}$  mode to smoothly connect to the  $A_g$  mode there must be some softening. Figure 5 shows ambient pressure values obtained from Iliev *et. al.*<sup>22</sup> for all four Raman active modes in rutile  $\text{CrO}_2$  as dark triangles. It is clear that a smooth curve can be drawn

between the ambient pressure values and our data for the  $E_g$ ,  $A_{1g}$ , and  $B_{2g}$  modes, but not for the  $B_{1g}$  mode. This is further evidence that  $\beta$ - $\text{CrO}_2$  takes the  $\text{CaCl}_2$  since softening of the  $B_{1g}$  has been seen in many of the rutile- $\text{CaCl}_2$  transitions.<sup>14,18,15</sup> It should again be noted that the unidentified peak showing up at 33 GPa, marked with an asterisk in Fig. 6, shows a pressure-induced shift consistent with the rest of the identified modes.

### 3. Discussion

The present x-ray data reveal that the rutile-to- $\text{CaCl}_2$  transition in  $\text{CrO}_2$  is a strain-driven, 2<sup>nd</sup>-order distortive phase transition. The crystal structures of both phases (see Fig. 1) consist of distorted edge-sharing  $\text{CrO}_6$  octahedra where the degree of distortion increases as you move from  $\alpha$ - $\text{CrO}_2$  to  $\beta$ - $\text{CrO}_2$ . For example, at ambient conditions the four equatorial Cr-O bonds in the [110] plane are at 1.917 Å and lie roughly along the c-axis while the other two apical Cr-O bonds in the [1-10] plane are at 1.882 Å and lie parallel to the ab-plane. At the onset of the transition at  $12.4 \pm 3$  GPa the disparity in Cr-O distances increases to 1.930 Å for the equatorial bond and 1.795 Å for the apical bond. This local strain arising from the large disparity in bond lengths along the c-axis and ab-plane results in a large compressibility along the c-axis with respect to the a- and b-axes (see Fig. 2) and an increase of the O-O contact distance to 2.568 Å for  $\beta$ - $\text{CrO}_2$  from the relatively short 2.488 Å in  $\alpha$ - $\text{CrO}_2$ . This short O-O distance in  $\alpha$ - $\text{CrO}_2$  may induce the softening of the  $B_{1g}$  mode inferred from the present Raman data, shown in Fig. 6, and cause a mechanical instability of the rutile structure.<sup>24,25</sup>

It is often difficult to correctly determine the order of a phase transition through structural measurements alone. Recall that the splitting of the (101) diffraction peak into (101) and (011) peaks is seen clearly at 12.8 GPa. However, broadening of the (101) peak before 12.8 GPa was also detected which could indicate a continuous second-order transition that begins before 12.8 GPa. This is illustrated in Fig. 3 where a discontinuity in the lattice parameters is shown at 12.8 GPa, however extrapolation of the *a*- and *b*- axis curves from  $\beta$ - $\text{CrO}_2$  back to the *a*-axis from  $\alpha$ - $\text{CrO}_2$  could indicate a continuous transition beginning as low as 10.8 GPa. Indeed, in many other rutile-type oxides<sup>13,17,12</sup> the transition to the  $\text{CaCl}_2$  structure has been shown to be second-order with the

spontaneous strain,  $e_{ss} = (a - b)/(a + b)$ , as the order parameter. According to Landau's theory of second-order phase transitions, the order parameter should be proportional to  $(P - P_c)^{1/2}$ . To examine this possibility, we have plotted  $e_{ss}^2$  vs. pressure in Fig. 7(a). Our data appear very linear up to 25 GPa with a fit to a straight line giving a value of  $P_c = 12.2$  GPa. Above 25 GPa, however, strong deviations from linearity are observed. The splitting of the  $E_g$  mode in rutile materials has been shown to be directly proportional to the spontaneous strain and should therefore also follow a  $(P - P_c)^{1/2}$  scaling.<sup>26</sup> The square of this splitting is plotted in Fig. 7(b). We again see good linearity up to 25 GPa, giving a value of  $P_c = 10.0$  GPa, above which we see deviations. The agreement with  $(P - P_c)^{1/2}$  below 25 GPa suggests that this is indeed a second-order transition. Although this scaling only rigorously applies near the transition pressure, the deviations at 25 GPa coincide with the new Raman peak observed at 33 GPa and the change in compressibility of the c-axis, and could indicate the appearance of a new phase. However, no indication of a second structural phase transition was found in the x-ray diffraction data. Therefore, further experiments are needed to make a solid conclusion.

The lower value of  $P_c$  obtained from our Raman data, compared to x-ray, is likely due to the use of different pressure media: argon for Raman and He for x-ray diffraction. Argon is known to provide slightly less hydrostatic conditions than He and therefore could have forced the transition to occur at a lower pressure during the Raman experiment. In addition, the larger compressibility of the c-axis observed in  $\alpha$ -CrO<sub>2</sub> using mineral oil compared to that obtained using He, shown in Fig. 2, is also suggestive of a greater strain than in He. It has been shown by Haines *et. al.*<sup>17</sup> that the rutile- $\rightarrow$ CaCl<sub>2</sub> transition is very sensitive to non-hydrostatic stress and the use of non-hydrostatic pressure media can lower the transition pressure by as much as 8 GPa for SnO<sub>2</sub>. Therefore, we place the transition at  $12 \pm 3$  GPa based on the first appearance of a clear splitting of the diffraction lines with  $h \neq k$  and estimate the experimental uncertainty to be  $\sim 3$  GPa due to the discrepancy in  $P_c$  discussed above.

It is interesting to note that extrapolated zero-pressure bulk modulus of  $\beta$ -CrO<sub>2</sub> is lower than that of  $\alpha$ -CrO<sub>2</sub> going from  $B_0 = 239 \pm 2$  to  $B_0 = 162 \pm 2$  across the phase transition (see Fig. 3 and Table I). Lattice softening is not uncommon for strain-driven distortive-type transitions at high pressures, as seen in materials like ReO<sub>3</sub> and UO<sub>3</sub> where the softening occurs as a result of “buckling” of the linear Re-O bonds.<sup>27,28</sup> As previously discussed and shown in Fig. 3, the change in volume compressibility comes largely from an increase in compressibility of the c-axis, not from a change in compressibility of the ab-plane as evident from the area conserving parameter  $\sqrt{ab}$ . A similar lattice softening has also been seen during the high-pressure rutile  $\rightarrow$   $\alpha$ -PbO<sub>2</sub> transition in TiO<sub>2</sub> and PbO<sub>2</sub> which also involves a large change in the compressibility of the c-axis.<sup>19,29</sup> In these materials the change in compressibility is due to the way the O-octahedra link along the c-axis, forming zig-zag edge-sharing chains instead of straight edge-sharing chains as in rutile. This increases the number of distortion mechanisms and hence a larger compressibility. The rutile-CaCl<sub>2</sub> transition, however, does not alter the way O-octahedra link along the c-axis and may therefore need an alternative explanation for the lattice softening.

The tetragonal distortion (apical Cr-O bond is shorter than the equatorial bonds) of the CrO<sub>6</sub> octahedra introduced in  $\alpha$ -CrO<sub>2</sub> splits the doubly degenerate  $e_g$  molecular orbital into  $a_{1g}$  and  $b_{2g}$  states and splits the triply degenerate  $t_{2g}$  orbital into  $b_{2g}$  and  $e_g$ .<sup>30</sup> The orthorhombic distortion in  $\beta$ -CrO<sub>2</sub> further splits this latter  $e_g$  orbital into  $b_{2g}$  and  $b_{3g}$  orbitals. As a result, the two unpaired d-electrons in  $d^2$  CrO<sub>2</sub> can be paired up in the lowest energy d-orbital, either  $b_{2g}$  or  $b_{3g}$ , in a sufficiently strong crystal field. This would be equivalent to removing the exchange splitting of the up-spin and down-spin  $d$ -states and increasing the metallic character of CrO<sub>2</sub>. Lattice softening due to changes in the electronic structure has been seen in a variety of materials. In the monochalcogenides of the rare-earths, such as TmTe, the anomalous increase in compressibility with pressure is attributed to continuous 4f-5d electron promotion, resulting in a semiconductor-metal transition.<sup>31</sup> Shock experiments on liquid D<sub>2</sub> indicate a significant increase in compressibility accompanying the insulator-metal transition.<sup>32</sup> We therefore postulate

that the increase in compressibility of  $\text{CrO}_2$  at 12 GPa may be due to an electronic transition from half-metal to metal. Recent electronic structure calculations support this conjecture by showing that the density of state is much more sensitive to changes in the c-axis than either the a- or b-axis.

The transition observed in the present study is in accordance with other  $\text{MO}_2$ -type transition metal or group-IV dioxides taking the rutile structure. For example, rutile-type  $\text{MnO}_2$  undergoes a phase transition at 0.3 GPa to the  $\text{CaCl}_2$  structure and possibly another phase transition around 46 GPa to an unknown cubic phase.<sup>12</sup> Other materials often undergo post-rutile phase transition to structures such as  $\alpha\text{-PbO}_2$ ,  $\alpha\text{-cristobalite}$ , etc. Table II summarizes the results for many  $\text{MO}_2$  compounds. To compare  $\text{CrO}_2$  with the rutile-type compounds at high pressure and to gain insight into the systematics of these transitions we have plotted the metallic ion radii vs. transition pressure in Fig. 8(a). It should be noted that the structural results from Table II were taken from Bolzan *et al*<sup>33</sup>, however the values for the ionic radii were taken from Shannon and Prewitt<sup>34</sup>. The values used in [33] are those obtained by Ahrens which do not account for coordination number and spin state and, consequently, do not give the correct values for the anion-cation distances when added together. We see strong systematics in the group IV metal dioxides showing increasing transition pressure with decreasing anion radius. The transition metals, however, show much more complex behavior.

To elucidate the connection between transition pressure and ambient pressure crystal structure parameters we have also calculated the degree of  $\text{MO}_6$  octahedra distortion at ambient pressure, defined as  $|(r_1 - r_2)/(r_1 + r_2)|$  where  $r_1 \equiv$  apical M-O distance and  $r_2 \equiv$  equatorial M-O distance. The values are plotted as a function of transition pressure in Fig. 8(b). It suggests that a higher degree of distortion leads to a dramatic increase in the stability range of the rutile structure.  $\alpha\text{-CrO}_2$ , with an ambient pressure value of 0.00916 agrees well with the other transition-metal compounds. It should also be noted that although the group-IV compounds and transition-metal compounds both follow a nearly linear trend, the line of transition-metal compounds is below that of group-IV. We can try to understand this behavior by looking at the  $\text{B}_{1g}$  vibrational mode frequency,

$\nu_{B_{1g}}$ , at ambient pressure for the various  $MO_2$  compounds as a function of transition pressure. This is plotted in Fig. 8(c). We can see that an increased distortion of the  $MO_6$  leads to an increase in  $\nu_{B_{1g}}$ . Since the rutile- $CaCl_2$  transition is driven by a mechanical instability with the same symmetry as the  $B_{1g}$  mode, demonstrated by softening of this mode, a material with a higher ambient pressure value for  $\nu_{B_{1g}}$  may take longer to transform, leading to a higher value for  $P_c$ . The fact that for a given distortion, the values for  $\nu_{B_{1g}}$  for the transition metal oxides are systematically lower, leading to lower values for  $P_c$ , may be electronic in nature. The bonding between M-O in the transition metal oxides is dominated by its partially-filled  $d$ -orbitals where in the group IV compounds, this same bonding has predominantly  $p$ -character.

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### Figure Captions:

**FIG. 1.** (a) The edge-sharing octahedra of the rutile structure along the  $c$ -axis. (b) Shows rutile-structured  $\alpha$ -CrO<sub>2</sub> ( $P4_2/mnm$ ,  $Z=2$ ,  $a = b = 4.421$  Å,  $c = 2.916$  Å,  $u = .301$ ) at ambient conditions projected onto the  $ab$ -plane with Cr<sup>+4</sup> ions in black and O<sup>-2</sup> ions in white. (c) Shows  $\beta$ -CrO<sub>2</sub> ( $Pnmm$ ,  $Z=2$ ,  $a = 4.425$ ,  $b = 3.987$ , and  $c = 2.683$ , and  $u_x=0.371$  and  $u_y=0.263$ ) at 50.4 GPa. The transition from  $\alpha$ -CrO<sub>2</sub> to  $\beta$ -CrO<sub>2</sub> involves an orthorhombic distortion and a rotation of the CrO<sub>6</sub> octahedra about the  $c$ -axis.

**FIG. 2.** (Color Online) Rietveld refinement of CrO<sub>2</sub> x-ray diffraction data taken at 7.7 and 14.0 GPa. Open circles show experimental data while red and blue lines show calculated spectra and difference spectra, respectively. Short vertical lines shows position of diffraction lines. (a) shows the structural refinement of rutile  $\alpha$ -CrO<sub>2</sub>, space group  $P4_2/mnm$ , while (b) shows the structural refinement of orthorhombic  $\beta$ -CrO<sub>2</sub> in the CaCl<sub>2</sub> structure, space group  $Pnmm$ . Only the strongest  $(hkl)$ 's are labeled.  $(hkl)$ 's shown in bold represent those diffraction lines with  $h \neq k$  which were split during to the orthorhombic distortion from tetragonal  $P4_2/mnm$  to orthorhombic  $Pnmm$ . The values  $R_{wp}$ ,  $R_p$ , and expected  $R_{wp}$  were calculated without contributions from the background fit.

**FIG. 3.** Lattice constants of CrO<sub>2</sub> as a function of pressure. Open and closed circles represent data taken with Helium and mineral oil as a pressure medium. Dark triangles are data obtained by Cloud *et. al.*<sup>11</sup>. Crosses represent the area conserving quantity  $\sqrt{ab}$ . Vertical dotted line at 12 GPa shows transition from rutile  $\alpha$ -CrO<sub>2</sub> to orthorhombic  $\beta$ -CrO<sub>2</sub>.

**FIG. 4.** Pressure vs. Volume data for CrO<sub>2</sub>. Dotted vertical line shows transition from rutile  $\alpha$ -CrO<sub>2</sub> to orthorhombic  $\beta$ -CrO<sub>2</sub>. Dark circles are data collected using a He pressure medium and dark triangles were collected using mineral oil as the pressure medium.

Dotted vertical line denotes transition pressure of  $12 \pm 3$  GPa. Error bars are shown when uncertainties exceed symbol width. Various fits are shown using the Vinet and Birch-Murnaghan equations of state, both with and without fixing  $B_0'=4$ . The numerical results are summarized in Table 1.

**FIG. 5.** Raman spectra of  $\text{CrO}_2$  at 532 nm excitation at various pressures. At 12.4 GPa the broadening of the  $E_g$  mode due to a splitting and the appearance of a new mode at  $470 \text{ cm}^{-1}$  are consistent with a phase transition from rutile to  $\text{CaCl}_2$  structures. We also see the appearance of the Raman active  $A_g$  mode in  $\text{CaCl}_2$  as shown at 19.5 GPa. The asterisk marks an unidentified peak occurring at 32 GPa and persisting up to the highest pressure obtained during this experiment. A broad background has been subtracted from all spectra. The cross marks an intermittent peak caused by a combination of the holographic notch filters and the background subtraction and does not shift consistently with pressure.

**FIG. 6.** Plot of  $\text{CrO}_2$  phonons vs. pressure in the rutile and  $\text{CaCl}_2$  structures. Dark triangles show ambient pressure values obtained by Iliev *et.al.*<sup>22</sup> on single crystal  $\text{CaCl}_2$ . Dark circles represent our data. Dotted vertical line at 12 GPa denotes the transition from tetragonal  $\alpha\text{-CrO}_2$  to orthorhombic  $\beta\text{-CrO}_2$  derived from our experimental data.

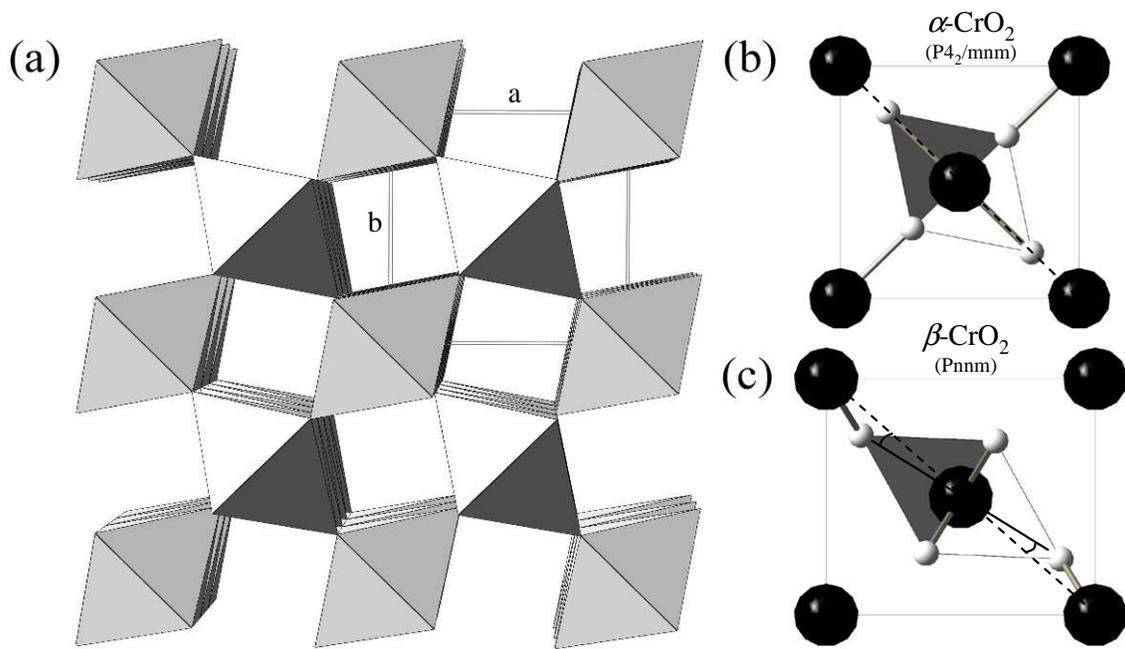
**FIG. 7.** Plot of the square of the (a) spontaneous strain, defined as  $(a-b)/(a+b)$ , and (b)  $E_g$  phonon splitting, defined as  $(\nu_1 - \nu_2)/(\nu_1 + \nu_2)$ , vs. pressure. Dotted lines show a linear fit of the form  $A^2(P - P_c)$  up to 25 GPa giving  $P_c = 10.00$  GPa for (a) and  $P_c = 12.20$  GPa for (b). Deviations from linearity are clear above 25 GPa.

**FIG. 8.** (a) Metallic ion radii for select  $\text{MO}_6$  compounds vs. transition pressure,  $P_c$ . Open squares show group-IV oxides and dark squares show transition-metal oxides. Dotted line serves as a guide to the eye to show the trend of increasing transition pressure with decreasing anion radii. (b) shows plot of the ambient pressure  $\text{MO}_6$  distortion, defined as  $|(a-b)/(a+b)|$  where  $a \equiv$  apical M-O distance and  $b \equiv$  equatorial M-O

distance, vs. transition pressure(left axis, squares) and  $B_{1g}$  mode frequency(right axis, triangles). Light and dark squares represent the group IV and transition metal oxides, respectively. Dashed lines are linear fits showing increasing transition pressure with increasing  $MO_6$  distortion. Inset (c) shows increase of  $B_{1g}$  mode frequency with increasing distortion.

**TABLE I.** Summary of numerical results from various equation of state fits to our experimental PV data. Numbers shown without error denote values that were fixed during the fitting procedure.

**TABLE II.** Rutile to  $CaCl_2$  transformation pressures and ambient pressure anion radii, degree of  $MO_6$  distortion, and  $B_{1g}$  mode frequencies for various metal oxides. <sup>a</sup>Anion radii obtained from Ref. [34] for the 4<sup>th</sup> oxidation state and 6-fold coordination. <sup>b</sup>Structural information for metal oxides at ambient conditions is summarized in Ref. [33]. <sup>†</sup>Transition pressure for rutile to  $\alpha$ - $PbO_2$  in  $TiO_2$ .



**FIG. 1.**

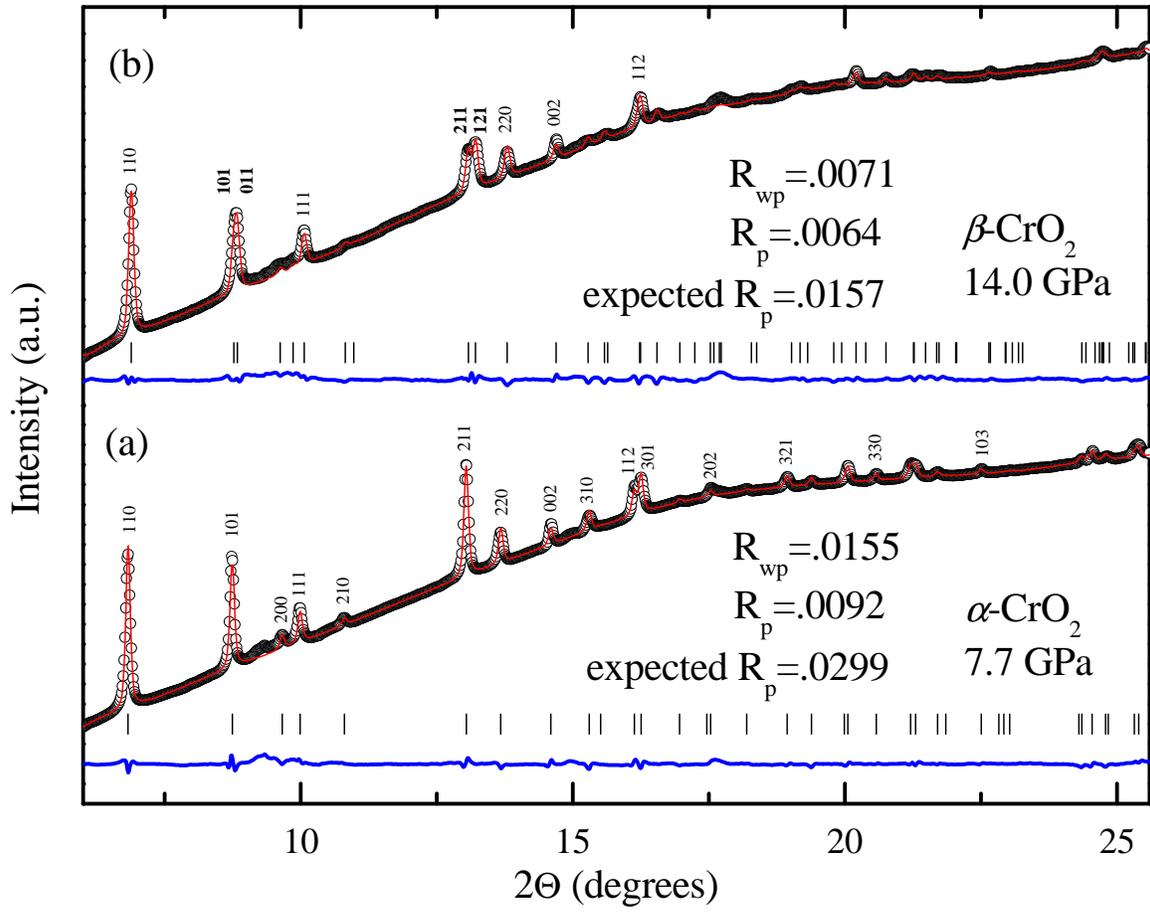


FIG. 2.(color online)

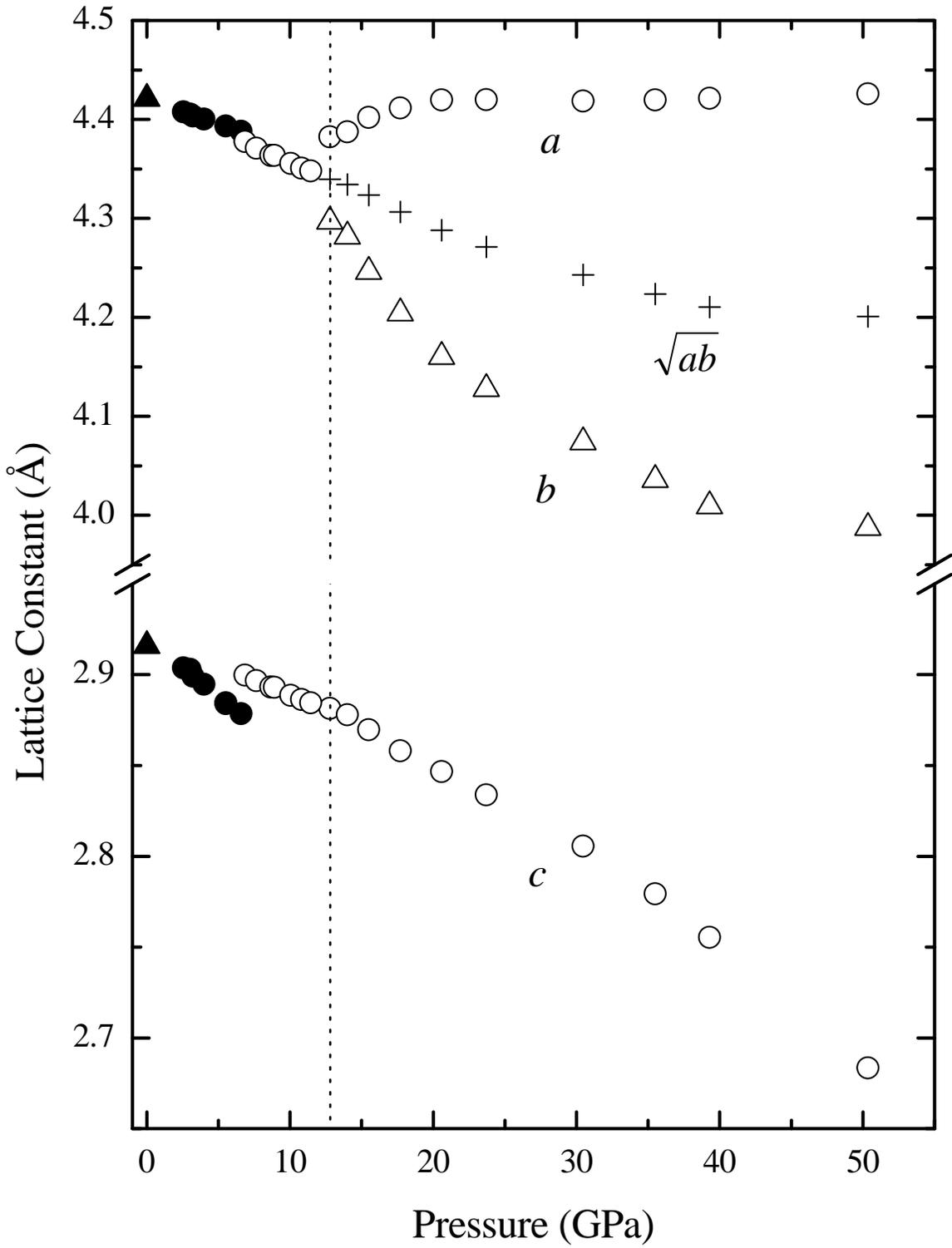


FIG. 3.

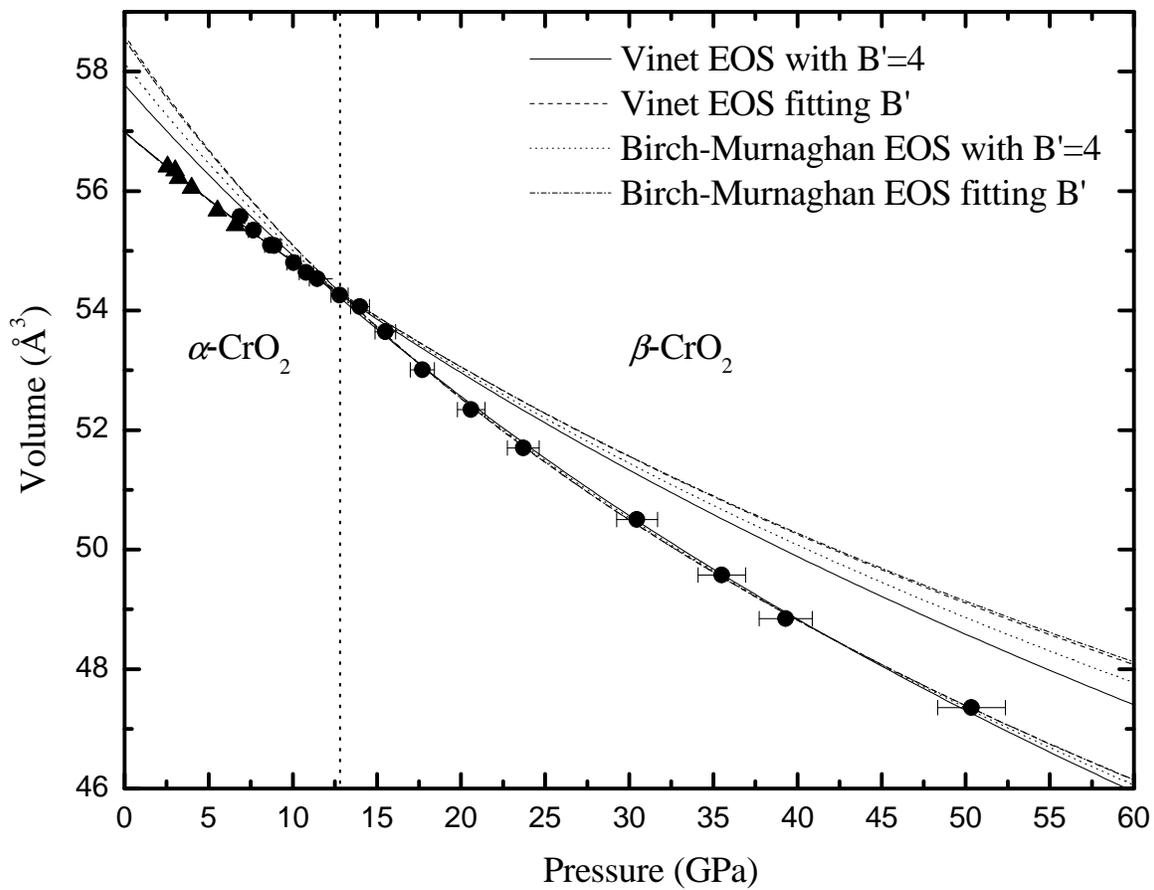


FIG. 4.

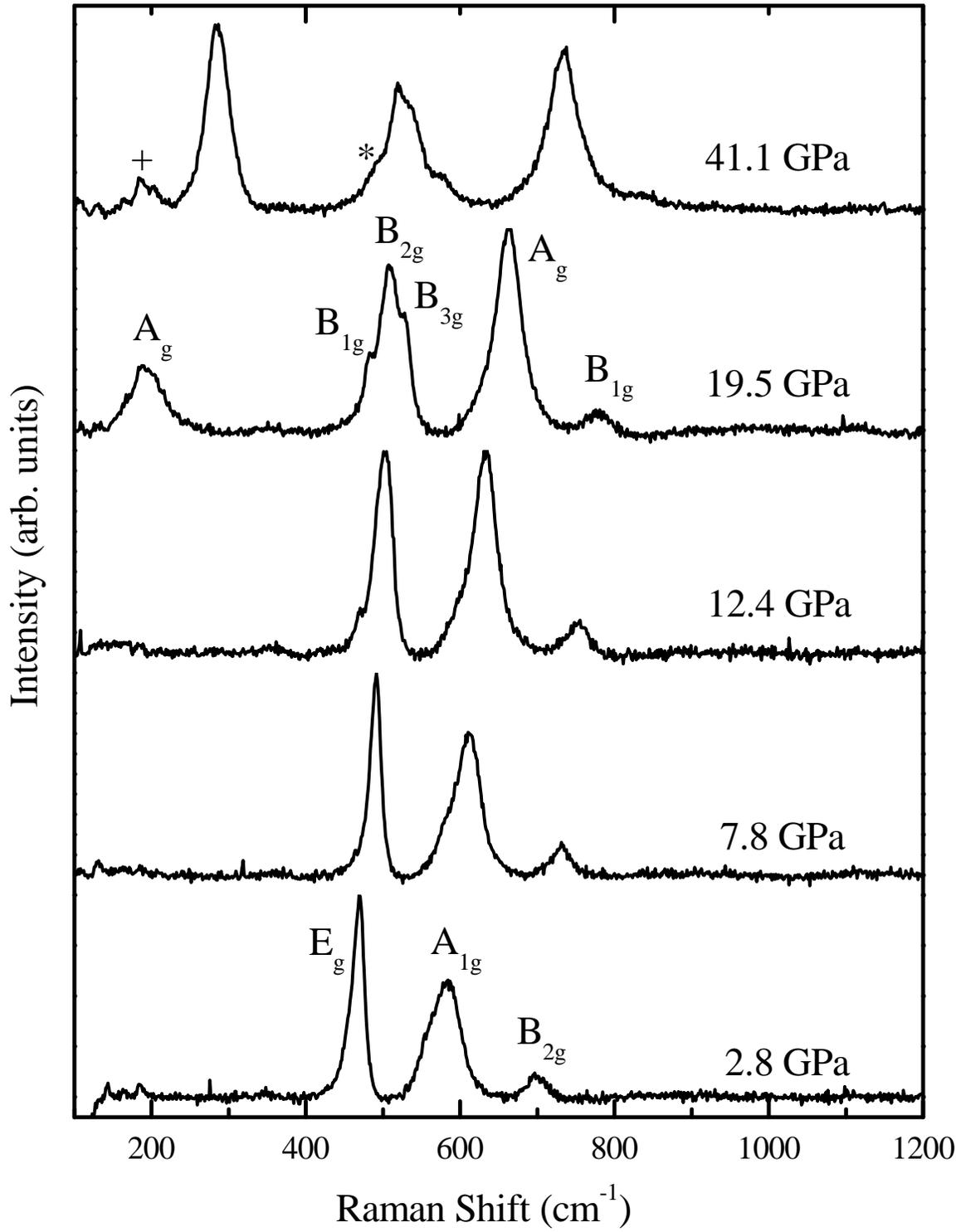


FIG. 5.

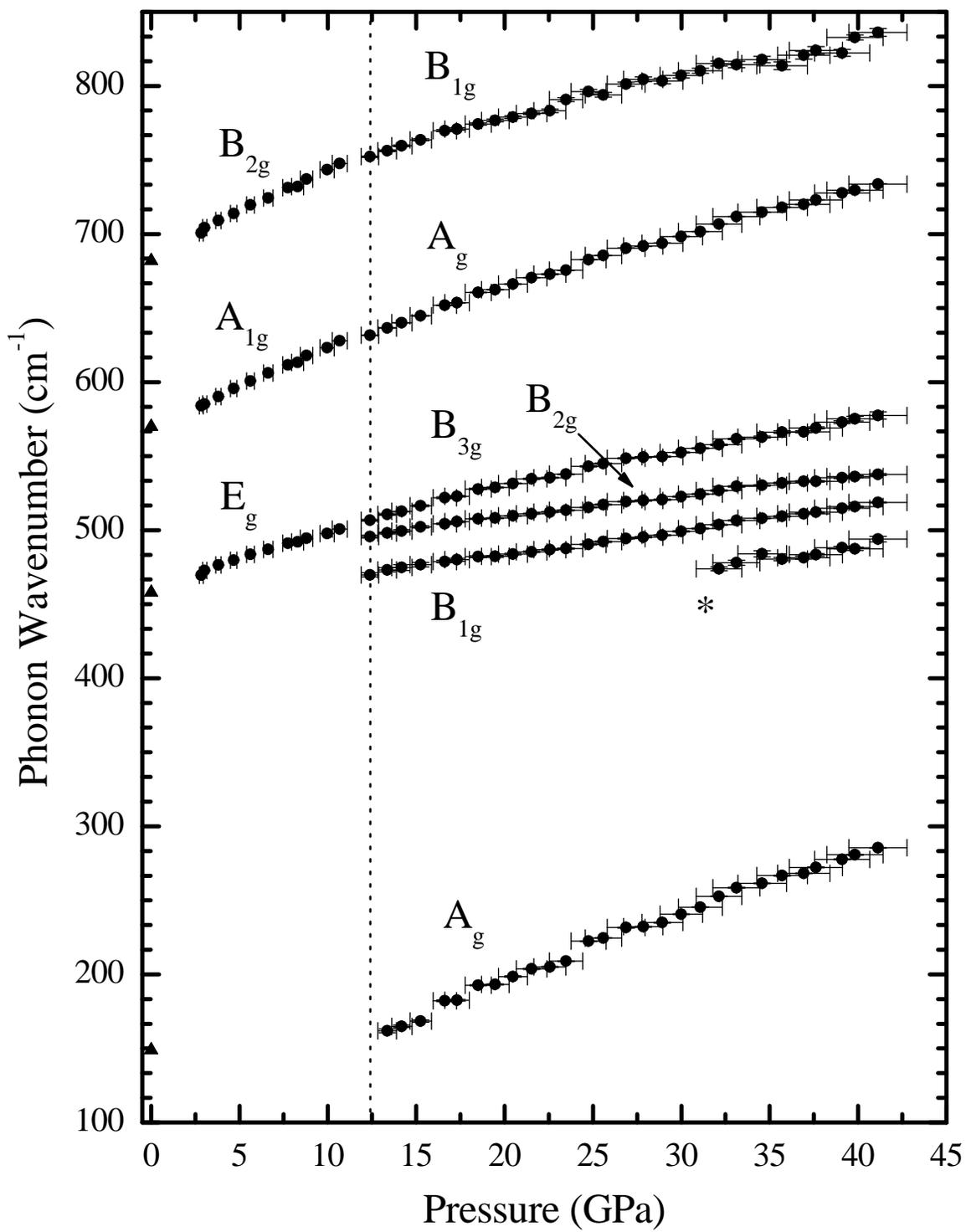


FIG. 6.

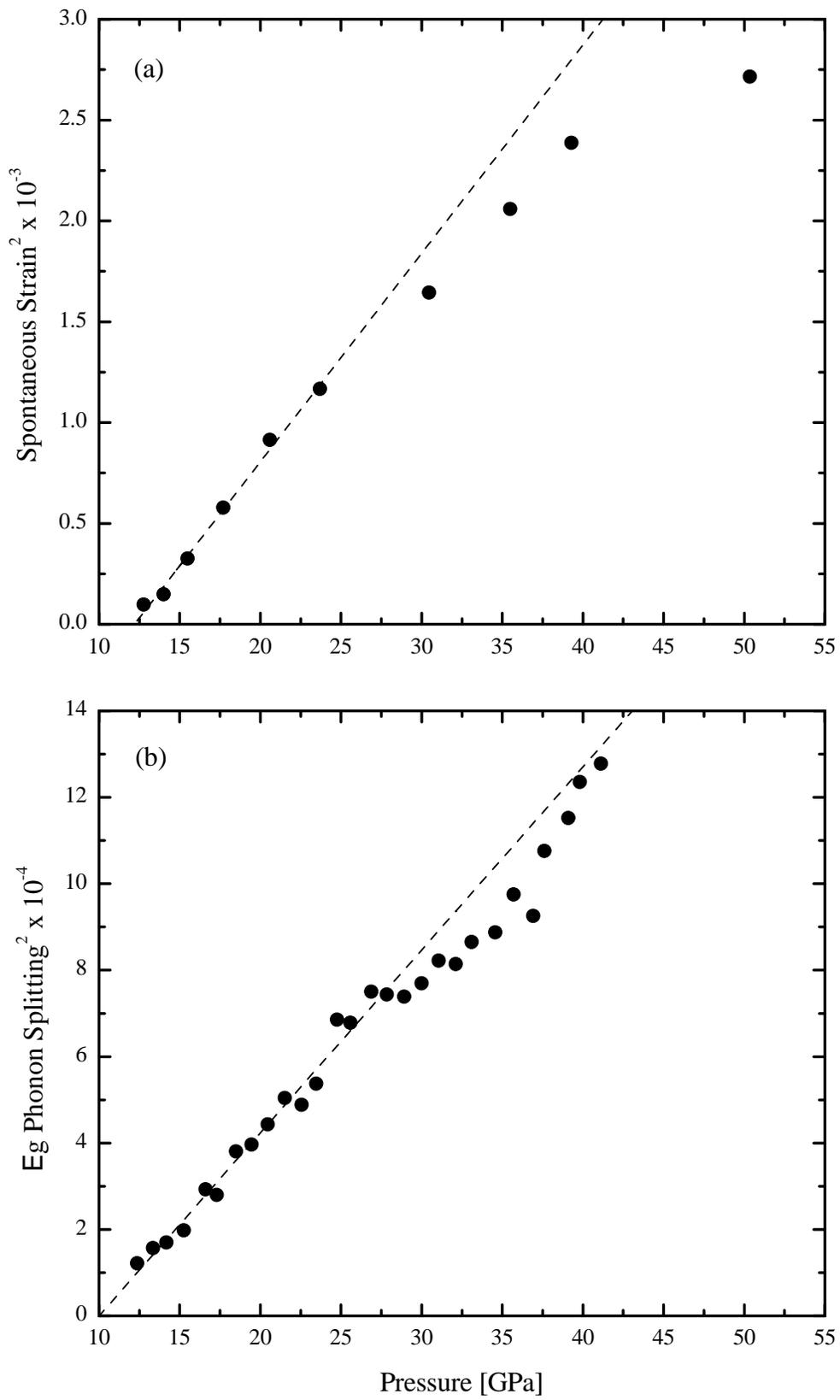


FIG. 7.

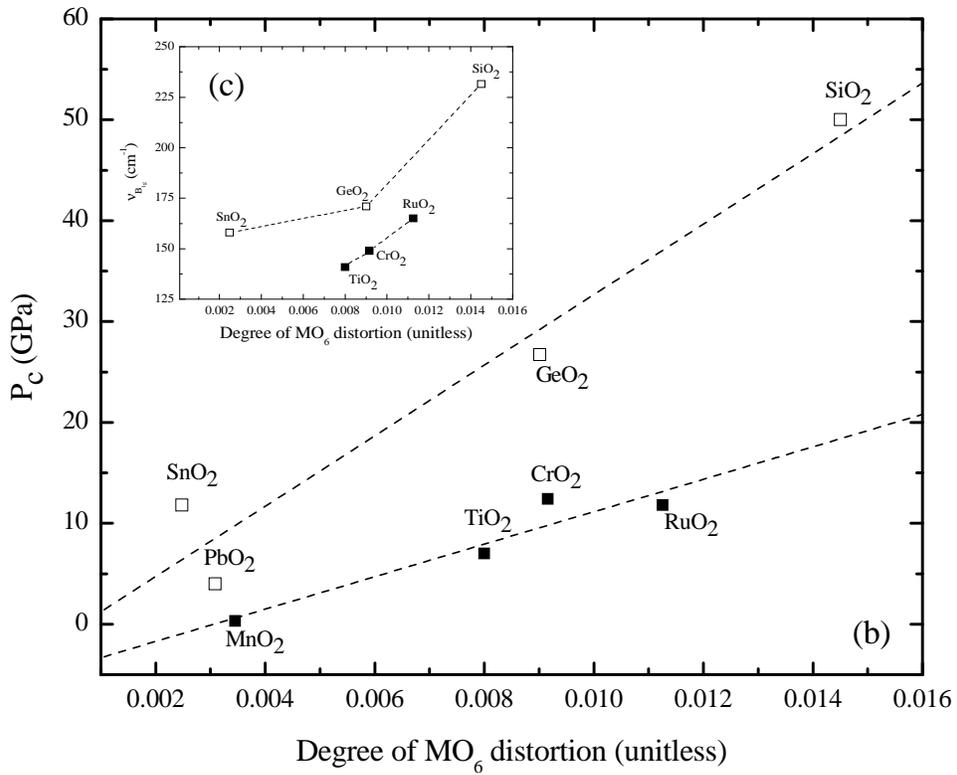
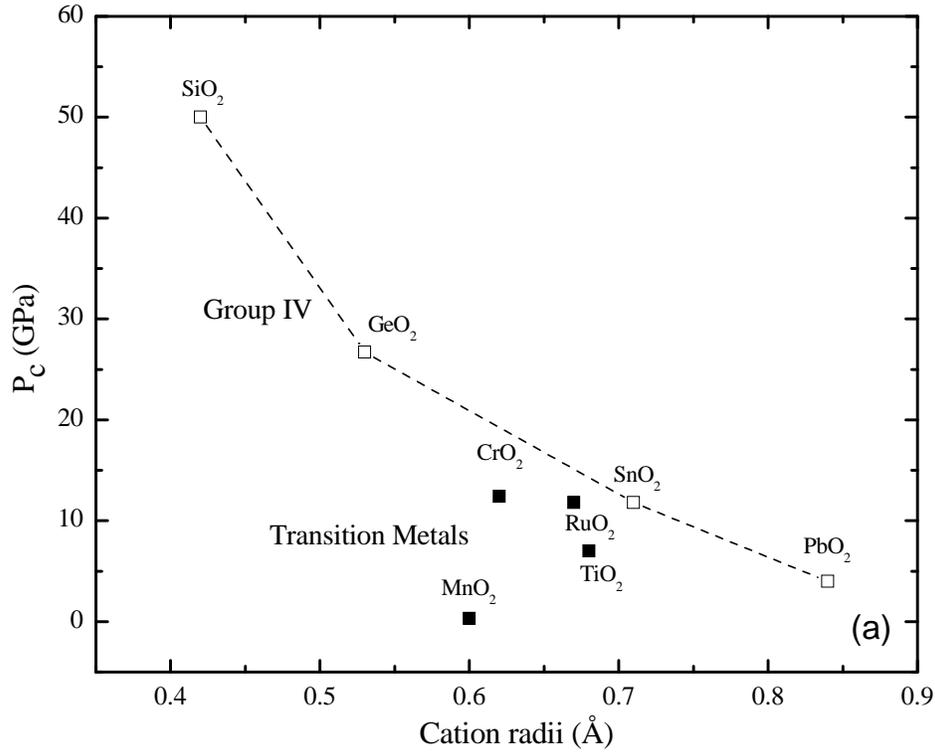


FIG. 8.

Phase	Birch-Murnaghan			Vinet		
	$B_0$ (GPa)	$B_0'$	$V_0$ (Å <sup>3</sup> )	$B_0$ (GPa)	$B_0'$	$V_0$ (Å <sup>3</sup> )
I	$239 \pm 2$	4.0	56.99	$242 \pm 2$	4.0	56.99
I	$235 \pm 10$	$5 \pm 2$	56.99	$235 \pm 10$	$6 \pm 2$	56.99
II	$162 \pm 2$	4.0	$58.1 \pm .1$	$181 \pm 3$	4.0	$57.8 \pm .1$
II	$143 \pm 16$	$4.8 \pm .7$	$58.5 \pm .4$	$138 \pm 16$	$5.8 \pm .7$	$58.6 \pm .4$

**TABLE I.**

MO <sub>2</sub> Comound	Transition Pressure (GPa)	Anion radii <sup>a</sup> (Å)	MO <sub>6</sub> <sup>b</sup>	B <sub>1g</sub> frequency (cm <sup>-1</sup> )
TiO <sub>2</sub> <sup>†</sup>	7	.745	0.008	141
CrO <sub>2</sub>	12.2	.69	0.00916	149
MnO <sub>2</sub>	.3	.68	0.00345	-
RuO <sub>2</sub>	11.8	.76	0.01126	165
SiO <sub>2</sub>	50	.54	0.0145	232
GeO <sub>2</sub>	26.72	.68	0.00901	171
SnO <sub>2</sub>	11.8	.83	0.00248	158
PbO <sub>2</sub>	4	.915	0.00309	-

**TABLE II.**